

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number
WO 2004/053003 A1

(51) International Patent Classification⁷: C09D 11/00,
7/00, C07F 9/11, 7/28

(21) International Application Number:
PCT/GB2003/005356

(22) International Filing Date:
10 December 2003 (10.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0228887.6 11 December 2002 (11.12.2002) GB

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT,
RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

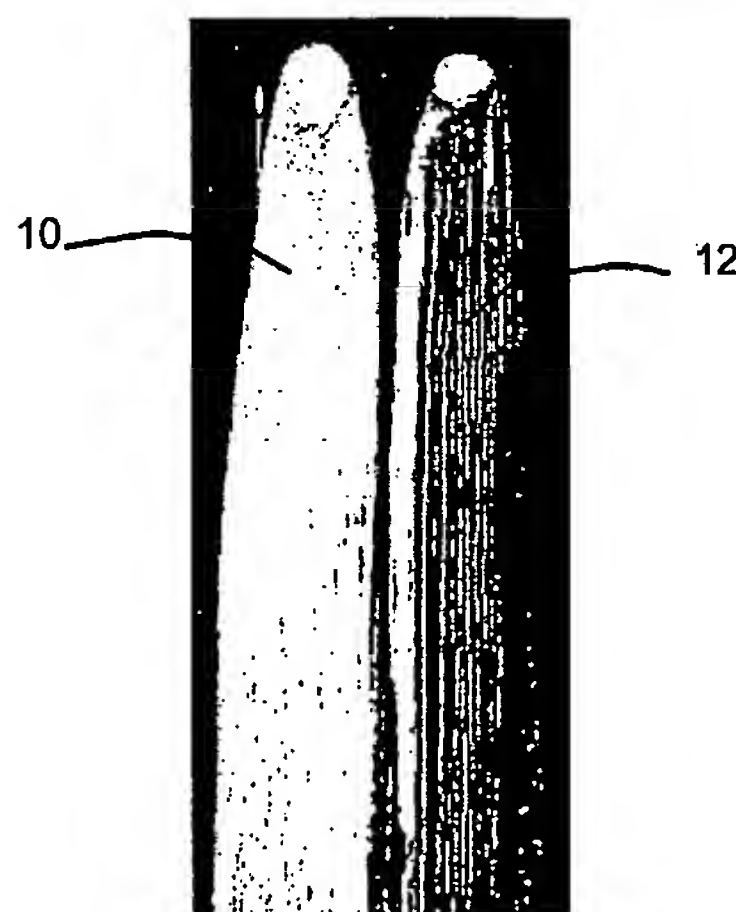
(84) Designated States (*regional*): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

[Continued on next page]

(54) Title: ADHESION PROMOTING COMPOUND AND COMPOSITION INCORPORATING SAME



(57) Abstract: The invention comprises an adhesion promoter, a coating and a printing ink containing the adhesion promoter for im-
proving the adhesion of the ink or coating to a substrate. The adhesion promoter comprises the reaction product of an organometallic
compound selected from a metal halide, alkoxide, condensed alkoxide or halo-alkoxide with an organophosphorus compound having
at least one P-OH group or its salt, the metal being selected from titanium and zirconium and the ratio of the total number of acid
P-OH group (or their salts) in the phosphate ester to number of moles of metal in the organometallic compound is from 3.1:1 to 8:1.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Adhesion Promoting Compound and Composition Incorporating Same

The present invention concerns adhesion promoting compounds for use in inks and coating compositions, in particular but not exclusively to enhance the adhesion between a printing ink
5 and a substrate, especially a plastics substrate, to which it is applied.

Adhesion promoting compounds are used in commercial inks formulations in order to enhance the adhesion between the ink and the substrate which is printed. Failure of adhesion leads to difficulties in the printing process or inadvertent removal of the print. Printing of plastics food
10 packaging is widespread and it is particularly important in such applications that the printed ink remains on the packaging and that parts of the ink composition do not contaminate the product.

Adhesion promoters based upon titanium compounds have been known and used commercially for many years. Whilst providing good adhesion between the ink and substrate,
15 simple titanium compounds such as titanium alkoxides have tended to impart undesirable yellow colour to the ink. GB-A-2161811 describes an adhesion promoter which is an organotitanate comprising the reaction product of a titanium orthoester and at least a monoalkyl phosphate (for example a mixture of a monoalkyl phosphate and a dialkyl phosphate) in which the alkyl group contains up to 6 carbon atoms and in which the total molar ratio P : Ti in the
20 product is less than 2. Such compositions provide efficient adhesion promotion with much less yellowing and have been successful commercially.

Organo titanates are widely used as crosslinkers for hydroxy-functional polymers (resins). When the resin is applied to a substrate and dried, cross linking occurs via a condensation
25 reaction between titanium alkoxy groups and polymer hydroxyls, resulting in the elimination of alcohol. The organo titanates improve adhesion to the substrate and improve the resistance properties of the coating – water, heat and solvent resistance. There is a tendency for cross-linking reactions to occur in the coating formulation during storage, or during mixing in the case of very reactive polymers. For some coatings applications a stable one-component system can
30 be formulated by incorporating alcohols in the solvent system to moderate the cross-linking action of the organo-titanate. The presence of alcohol suppresses these cross linking reactions in the liquid formulation and so stabilises viscosity (e.g. in nitrocellulose based printing inks and varnishes). In some applications, however, the addition of alcohol to the solvent is either undesirable, in order to minimise VOC levels, or impracticable due to incompatibility with
35 solvents or polymers in the formulation.

US-A-4433127 describes room-temperature curable silicone compositions comprising a silanol terminated polyorganosiloxane compound, a silyl isocyanate compound and a Ti-O-P bond-containing organic compound which has good storage stability, a short curing time, good

physical properties and which is not susceptible to discolouration. Some of the Ti-O-P containing compounds disclosed are tetra(dialkyl phosphato-) titanium compounds.

We have now found an adhesion promoter with improved properties.

5

According to the invention an adhesion promoter, for improving the adhesion of a coating composition to a substrate, comprises the product of reacting

- a) an organometallic compound selected from a metal halide, alkoxide, condensed alkoxide or halo-alkoxide or mixture thereof with
- 10 b) an organophosphorus compound having at least one P-OH group or a salt thereof, wherein the metal is selected from titanium and zirconium and the ratio of the total number of acid P-OH groups (or their salts) in the phosphate ester to the number of moles of metal in the organometallic compound is from 3.1 : 1 to 8 : 1.

- 15 According to a further aspect of the invention, we provide a printing ink comprising a resin, a solvent for said resin and an adhesion promoter, said adhesion promoter comprising the product of reacting

- a) an organometallic compound selected from a metal halide, alkoxide, condensed alkoxide or halo-alkoxide or mixture thereof with
- 20 b) an organophosphorus compound having at least one P-OH group or a salt thereof, wherein the metal is selected from titanium and zirconium and the ratio of the total number of acid P-OH groups (or their salts) in the phosphate ester to the number of moles of metal in the organometallic compound is from 3.1 : 1 to 8 : 1.

- 25 According to a further aspect of the invention, we provide a coating composition comprising a hydroxy-functional polymer, a solvent for said polymer and an adhesion promoter, said adhesion promoter comprising the product of reacting

- a) an organometallic compound selected from a metal halide, alkoxide, condensed alkoxide or halo-alkoxide or mixture thereof with
- 30 b) an organophosphorus compound having at least one P-OH group or a salt thereof, wherein the metal is selected from titanium and zirconium and the ratio of the total number of acid P-OH groups (or their salts) in the phosphate ester to the number of moles of metal in the organometallic compound is from 3.1 : 1 to 8 : 1.

- 35 The organophosphorus compound is preferably selected from a phosphate ester or a salt thereof comprising a dialkyl phosphate, a diaryl phosphate, a monoalkyl phosphate, a mono aryl phosphate or a mixture of two or more of a dialkyl phosphate, a diaryl phosphate, a monoalkyl phosphate and a mono aryl phosphate, a phosphonate ester or a salt thereof comprising an alkyl or aryl phosphonate or salts thereof, an alkyl or aryl pyrophosphate, an

alkyl or aryl phosphonic acid or alkyl or aryl ester thereof or a salt thereof, a dialkyl or aryl phosphinic acid or salt thereof. In all cases the organophosphorus compound contains a P-OH group, i.e. an acidic group or its salt. Suitable salts are alkali metal, alkaline earth or ammonium salts, e.g. Na^+ or NH_4^+ . The organophosphorus compound may be a mixture of
5 more than one said compound.

Preferably the ratio of the total number of acid P-OH groups (including those present as a salt) in the phosphate ester to the number of moles of metal in the organometallic compound is from 4 : 1 to 8 : 1, more preferably about 4 : 1. Although it is likely that a mixture of products results
10 from the above reaction, we have found, surprisingly, that it is not necessary to retain a labile metal-alkoxy bond in the adhesion promoting compound in order for it to be effective. In the prior art compositions, the ratio of P-OH groups to metal atoms has been 3 or less because, in the stoichiometric reaction between a phosphate ester and a titanium alkoxide, for example, each P-OH group replaces one alkoxide group with the consequent release of the
15 corresponding alcohol. It was thought that at least one labile (i.e. easily replaceable) alkoxide group should remain attached to the titanium atom to provide an active catalyst site for adhesion promotion. In making the adhesion promoters of the present invention, the ratio of P-OH groups to metal atoms is at least 3.1 : 1 and preferably at least 4 : 1 so that at least some of the titanium or zirconium forms 4 or more metal-O-P bonds so that all of the metal-O-alkyl
20 bonds are replaced. Surprisingly this compound performs well as an adhesion promoter for printing inks applied to plastic substrates. Compounds of this type are known, for example they are disclosed for use in curing silicone compositions in US-A-4433127. However their surprisingly good performance as adhesion promoting compounds has not hitherto been demonstrated.

25

The monoalkyl phosphate generally has a formula $(\text{R}^1\text{O})\text{PO}(\text{OH})_2$ in which R^1 represents an alkyl group containing up to 8 carbon atoms, more preferably up to 5 carbon atoms. The dialkyl phosphate if used generally has the formula $(\text{R}^2\text{O})(\text{R}^3\text{O})\text{PO}(\text{OH})$ in which R^2 and R^3 each represent an alkyl group usually containing up to 8 carbon atoms and preferably containing up
30 to 5 carbon atoms. Usually but not necessarily R^1 , R^2 and R^3 are identical. Preferably R^1 , R^2 and R^3 are selected from *n*-butyl, *iso*-propyl, ethyl, methyl, phenyl, amyl and ethyl-hexyl.

The phosphonate ester, phosphonic acid, phosphinic acid or salt thereof comprises an alkyl or aryl phosphonate, phosphonic acid or their salts and generally have a formula
35 $(\text{R}^4)_n\text{PO}(\text{OR}^5)_{2-n}(\text{OH})$, where R^4 and R^5 each represent a hydrogen atom or an aryl group or an alkyl group containing up to 8 carbon atoms and preferably containing up to 5 carbon atoms and *n* is 1 or 2.

Mixtures of phosphorus compounds such as a mixture of a monoalkyl (or monoaryl) phosphate and a dialkyl (or diaryl) phosphate may be used provided the total amount of P-OH groups present in the mixture is such as to provide that the ratio of P-OH groups to Ti atoms is from 3.1 : 1 to 8 : 1. Where the organophosphorus compound has two free P-OH groups it may
5 form two P-O-Ti bonds. These two bonds may involve the same metal atom or alternatively the monoalkyl or monoaryl phosphate may form bonds with two metal atoms to form a bridged or cross-linked structure. A compound having a large number of such cross-links is likely to be more viscous than a compound having significantly fewer cross-links and so it is desirable to restrict the amount of monoalkyl (or monoaryl) phosphate used to make the adhesion
10 promoting compound. When, for example, a mixture of monoalkyl and dialkyl phosphates are used, preferably the ratio of dialkyl phosphate to monoalkyl phosphate is at least 2 : 1, more preferably at least 4 : 1.

The metal compound selected from a metal halide, alkoxide, condensed alkoxide or halo-
15 alkoxide or mixture thereof is preferably a metal alkoxide having a general formula $M(OR)_4$ in which M is the metal and R is an alkyl group preferably having from 1 – 8 carbon atoms. Each R group may be the same as or different from the other R groups. Particularly suitable alkoxides include tetraisopropoxy titanium, tetra-n-butoxy titanium, tetraethoxy titanium, tetra-n-propoxy zirconium or tetra-n-butoxy zirconium.

20

The condensed alkoxides suitable for preparing the catalysts useful in this invention are typically prepared by careful hydrolysis of titanium or zirconium alkoxides and are frequently represented by the formula $R^6O[M(OR^6)_2O]_nR^6$ in which R^6 represents an alkyl group. Preferably, n is less than 20 and more preferably is less than 10. Preferably R^6 contains 1 to 6
25 carbon atoms and useful condensed alkoxides include the compounds known as polybutyl titanate and polyisopropyl titanate.

The adhesion promoter may be made by mixing together the metal compound with the phosphate ester. The alkyl phosphate is added carefully to the metal compound or vice-versa
30 to produce the desired reaction product. The reaction can be carried out at room temperature or with heating or cooling if desired and with stirring and cooling if necessary. If a mixture of phosphate esters is used, the dialkyl phosphate can be added separately or with the monoalkyl phosphate. The reaction of the phosphate ester with a titanium alkoxide results in the formation of an alcohol from the replaced alkoxide group. This alcohol may be removed from
35 the reaction mixture by distillation, normally under a vacuum but it may alternatively remain in the mixture. The adhesion promoter may be diluted in a solvent, which is typically an alcohol, ester or a mixture thereof.

The adhesion promoters are useful in printing inks. A printing ink typically consists of a

polymeric binder, a solvent, and usually a pigment and/or a dye. The adhesion promoter may also be useful in water-based inks which have a variety of compositions for example they may include aqueous solutions of water-soluble polymer together with a polymeric emulsion phase with the pigment or dye to give colour and opacity. Most inks also contain a variety of other
5 additives such as dispersants and surfactants. The adhesion promoter is required to promote cross-linking of the polymeric binder and adhesion of the ink to different substrates. The inks which are of particular interest are the flexographic or gravure inks in which the polymeric binder is cross-linkable and is dissolved in an appropriate organic solvent. Typical binders usable in such inks are those based on nitrocellulose or ester type modified celluloses, e.g.
10 cellulose acetate propionate or acrylic resins. Often such polymeric binders are employed in mixed form with polyamides, polyurethanes and/or other resins. The resin is not a silanol-terminated polyorganosiloxane compound of the type discussed in US 4,433,127. The ink usually contains one or more pigments and/or one or more dyes and typical pigments which can be used are the coloured inorganic pigments, white inorganic pigments and coloured
15 organic pigments. Organic dyes can be used to render the ink the appropriate colour and often are used in conjunction with an opacifying white inorganic pigment such as titanium dioxide. The adhesion promoter is added to the ink or coating composition in a known manner and typically at a concentration of from 0.05 to about 5%, preferably from 0.1 to 3% by weight of the ink composition. The adhesion promoter may be diluted in a suitable solvent before addition to
20 the ink or coating composition.

The adhesion promoter may simply be added to any other coating ingredients by mixing. For example, the adhesion promoter may be added to a conventional paint, varnish or other coating composition, including solvent-based and water-based paints such as emulsions, by adding it
25 to the paint or coating with stirring. The adhesion promoter is especially useful in solvent-based coatings and/or those in which a polymer having a high hydroxyl value is used, i.e. those coatings in which the hydroxyl-containing polymer is especially prone to premature cross-linking. The coating composition comprises a hydroxy-functional polymer which is typically an epoxy resin, a phenoxy resin or a nitrocellulose. The hydroxy-functional polymer is not a
30 silanol-terminated polyorganosiloxane compound of the type discussed in US 4,433,127. The adhesion promoter is preferably added in an amount of between 1 and 20% by weight of the total coating weight, more preferably between 3% and 12%, e.g. about 5 – 10% by weight.

The coating composition may be applied to a substrate by dipping, pouring, spraying, brushing
35 or by any other convenient method. It may be applied to a bare surface, e.g. a metal surface, or to another material which covers the surface, e.g. to a protective coating of e.g. iron phosphate on metal. The coating is generally cured at elevated temperature after application. Typically the coatings of the invention are cured at temperatures between 100 and 250 °C for a period of 5 – 30 minutes.

The invention is illustrated in the following examples:

Example 1

- 5 A solution of $\text{Ti}(\text{OPr}^i)_4$ (24.96g, 87mmol) in isopropyl alcohol (IPA) (20ml) was added slowly to a stirred solution of $(\text{BuO})_2\text{P}(\text{O})(\text{OH})$ (74.20g, 353mmol) in IPA (100ml). Bu represents n-butyl. The reaction was refluxed for one hour and the IPA was removed under reduced pressure to give $\text{Ti}[\text{OP}(\text{O})(\text{BuO})_2]_4$ as a colourless oil. The composition was confirmed by NMR spectroscopy and micro analysis (C : H : Ti).

10

Example 2

- A solution of a 2 : 1 molar mixture of $(\text{BuO})_2\text{P}(\text{O})(\text{OH})$ and $(\text{BuO})\text{P}(\text{O})(\text{OH})_2$ (68.90g, 359.9mmol) in IPA (10ml) was added drop-wise to a stirred solution of $\text{Ti}(\text{OPr}^i)_4$ (34.05g, 119.4mmol) in IPA (40ml). The reaction was heated a reflux for one hour and the IPA was removed under reduced pressure to give $\text{Ti}[\text{O}_2\text{P}(\text{O})(\text{BuO})][\text{OP}(\text{O})(\text{BuO})_2]_2$ as a colourless oil. The composition was confirmed by NMR spectroscopy.

15

Ink test

- The adhesion promoter compound to be tested was added to a TiO_2 base ink to give a mixture which contained 0.5-0.05 % of the compound by weight. Ink drawdowns were made on a, corona discharge treated, polypropylene or acetate film using a number 2 K-bar. Films were dried by making four passes over a silica bar at 60°C and then a tape adhesion test was made using 50mm wide red opaque Scapa tape "Cellulose Splice Red Tape Type 1112". Results are determined by the percentage ink remaining in the test area after removal of the adhesive tape.
- 25 Two adhesion promoting compounds to be compared are applied side-by-side to the same substrate film and a single strip of the adhesive tape is placed over both print samples together to ensure that the test conditions are identical. The amount of ink of each type remaining on the substrate can then be compared directly.

- 30 The ink adhesion test was performed as described using the adhesion promoter of Example 1 and also, as a comparison, $\text{Ti}[\text{OP}(\text{O})(\text{BuO})_2]_3[\text{OCH}(\text{CH}_3)_2]$ (both at 0.2% by weight). The results are demonstrated by the photographs shown in Fig 1, in which numeral 10 designates the part of the film coated with ink containing the adhesion promoter made in example 1 and numeral 12 designates the part of the film coated with the ink containing
- 35 $\text{Ti}[\text{OP}(\text{O})(\text{BuO})_2]_3[\text{OCH}(\text{CH}_3)_2]$. The photograph shows the film after the adhesive tape has been removed. The white parts show that ink remains on the film, whereas the black parts show the substrate film, the ink having been removed on the tape.

Example 3

40

3g $\text{Ti}[\text{OP}(\text{O})(\text{BuO})_2]_4$, as made in Example 1, was added to 50g of an epoxy resin (Araldite™ GZ 7488 V40 available from Vantico). The mixture was stirred by hand to homogenise. Some thickening was observed but the mixture remained mobile.

5 Example 4

A coating was formulated as in Example 3, using 3g of the Example 1 titanium composition and 50g of a phenoxy resin (INCHEMREZ PKHS-30PMA).

Drawdowns were made on iron phosphate-treated steel test panels using a No. 22 K applicator bar. The panels were placed in a fan-assisted oven at 232°C (450°F) for 5 minutes to cure the coating. After removing the panels from the oven and allowing to cool they were folded over through approximately 160 degrees. Adhesion was assessed by firming down a strip of pressure sensitive tape (Sellotape™) along the folded edge and then removing the tape using a sharp, jerky action. Both Example 3 and Example 4 samples gave 100% adhesion in the tape test i.e. no coating removed

MEK rub test

A folded strip of cloth, approximately 2-3 cm wide, was dipped into about 100 ml of 2-butanone (methyl ethyl ketone) in a beaker, so as to totally wet the cloth. The test panel was laid flat inside a fume cupboard and the soaked cloth was rubbed with moderately heavy finger pressure along the length of the test panel in a regular motion at an even rate such that around 100 double rubs (up and back) were carried out in one minute along the middle 100 mm or so of the panel. The effect of the rubbing was observed and the time was noted when removal of coating first started, when bare metal was first revealed and when the whole of the coating had been removed along the length of the panel. Solvent resistance was assessed by rubbing the flat area of the panel with mutton cloth soaked in MEK (methyl ethyl ketone). The coating was assessed visually after 100 and 200 double rubs.

The results were the same using both Example 3 and Example 4 coatings. After 100 MEK double rubs there was no damage. After 200 MEK double rubs both coatings showed slight damage to the surface

Claims

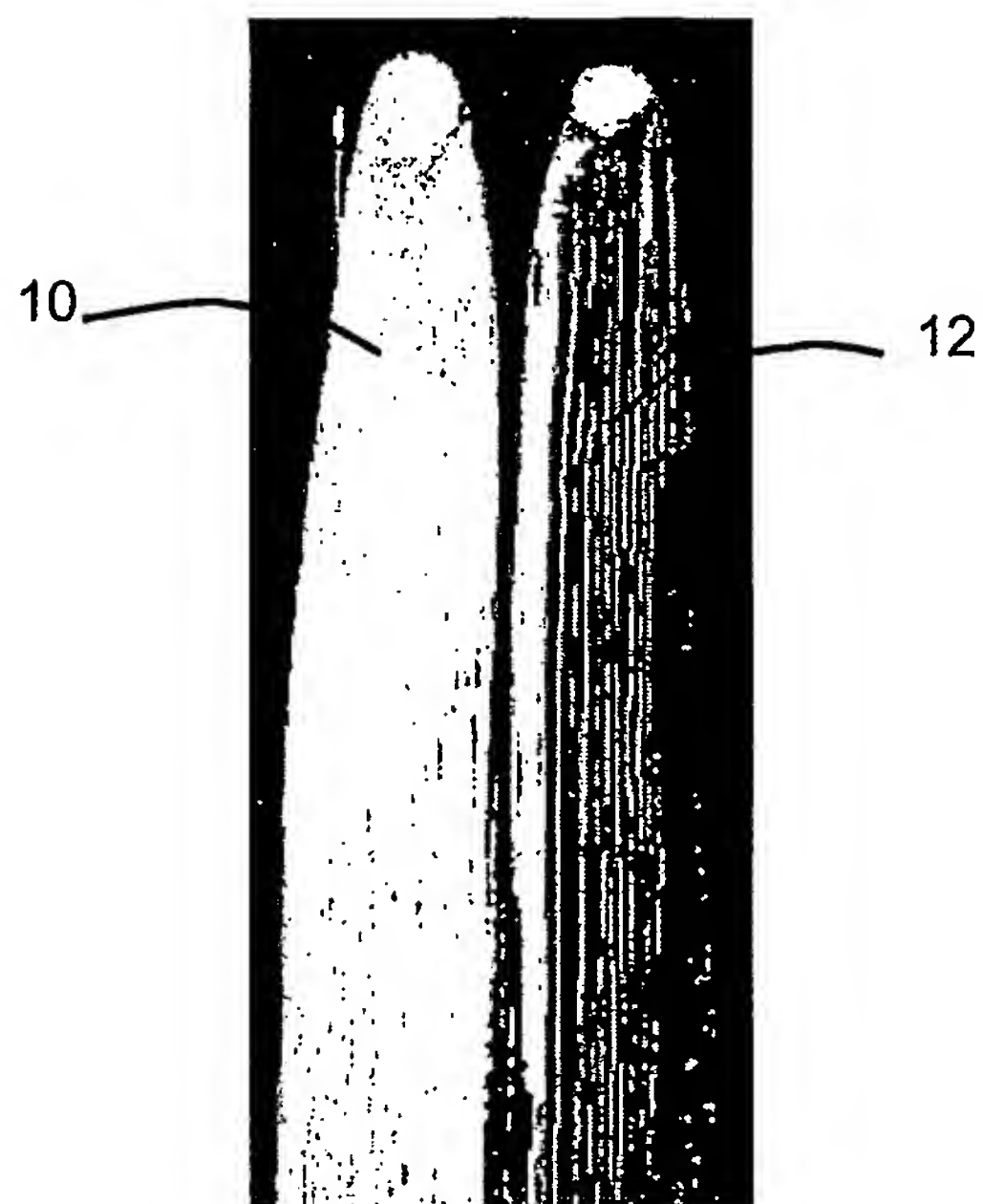
1. An adhesion promoter, for improving the adhesion of a coating composition to a substrate, comprising the product of reacting
 - a) an organometallic compound selected from a metal halide, alkoxide, condensed alkoxide or halo-alkoxide or mixture thereof with
 - b) an organophosphorus compound having at least one P-OH group or a salt thereof,wherein the metal is selected from titanium and zirconium and the ratio of the total number of acid P-OH groups (or their salts) in the phosphate ester to the number of moles of metal in the organometallic compound is from 3.1 : 1 to 8 : 1.
2. An adhesion promoter as claimed in claim 1, wherein said organophosphorus compound comprises a phosphate ester or a salt thereof comprising a dialkyl phosphate, a diaryl phosphate, a monoalkyl phosphate, a mono aryl phosphate or a mixture of two or more of a dialkyl phosphate, a diaryl phosphate, a monoalkyl phosphate and a mono aryl phosphate, a phosphonate ester or a salt thereof comprising an alkyl or aryl phosphonate or salts thereof, an alkyl or aryl phosphonic acid or alkyl or aryl ester thereof or a salt thereof, a dialkyl or diaryl phosphinic acid or salt thereof.
3. An adhesion promoter as claimed in claim 1 or claim 2, wherein said organophosphorus compound is a mixture of more than one compound.
4. An adhesion promoter as claimed in any one of the preceding claims, wherein the ratio of the total number of acid P-OH groups (including those present as a salt) in the organophosphorus compound to the number of moles of metal in the organometallic compound is from 3.1 : 1 to 8 : 1.
5. An adhesion promoter as claimed in any one of the preceding claims, wherein the organometallic compound comprises a tetra-alkoxy titanium or a tetra-alkoxy zirconium.
6. A composition for application to a surface comprising a resin or polymer, a solvent for said resin or polymer and an adhesion promoter as claimed in any one of claims 1 to 5.
7. A composition as claimed in claim 6, wherein said composition is a printing ink composition comprising a resin, a solvent for said resin and said adhesion promoter.
8. A composition as claimed in claim 6, wherein said adhesion promoter is present in an amount between 0.05 and 5% by weight of the total printing ink composition.

9. A composition as claimed in claim 6, wherein said composition is a coating composition comprising a hydroxy-functional polymer, a solvent for said polymer and said adhesion promoter.

10. A composition as claimed in claim 9, wherein said adhesion promoter is present in an amount between 1 and 20% by weight of the total coating weight.

1/1

Fig 1



INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/05356

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00 C09D7/00 C07F9/11 C07F7/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 507 437 A (FURUKAWA HISAO ET AL) 26 March 1985 (1985-03-26) claims; examples ---	1-10
P,X	WO 03 076546 A (DOW GLOBAL TECHNOLOGIES INC ;WU ZIYAN (US); HEBERER DANIEL P (US)) 18 September 2003 (2003-09-18) example 5; table 2 ---	1-10
X	US 5 116 411 A (O'NEILL MICHAEL W ET AL) 26 May 1992 (1992-05-26) example 1; table A ---	1-10
X	US 3 275 668 A (REVUKAS ANTHONY J) 27 September 1966 (1966-09-27) column 1, line 33 -column 2, line 47 --- -/--	1-5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

6 April 2004

Date of mailing of the international search report

15/04/2004

Name and mailing address of the ISA

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/05356

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 338 935 A (HESS FREDERICK G ET AL) 29 August 1967 (1967-08-29) claims; example 1 -----	1-5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/05356

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 4507437	A	26-03-1985	JP	1719548 C	14-12-1992
			JP	2061986 B	21-12-1990
			JP	59124954 A	19-07-1984
			DE	3370013 D1	09-04-1987
			EP	0117311 A1	05-09-1984
WO 03076546	A	18-09-2003	US	2003173026 A1	18-09-2003
			WO	03076546 A1	18-09-2003
US 5116411	A	26-05-1992	NONE		
US 3275668	A	27-09-1966	US	3231347 A	25-01-1966
US 3338935	A	29-08-1967	BE	677154 A	29-08-1966
			DE	1568247 A1	09-10-1969
			FR	1469933 A	17-02-1967
			GB	1135261 A	04-12-1968
			NL	6601433 A	07-08-1967
			US	3388978 A	18-06-1968
			US	3389082 A	18-06-1968